

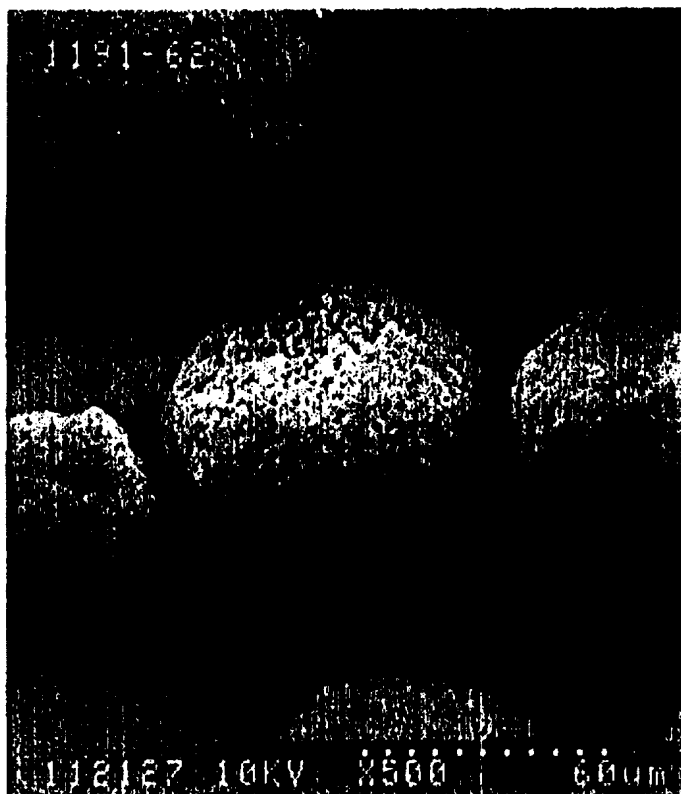


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<b>(21) International Application Number:</b> PCT/US97/11951 <b>(22) International Filing Date:</b> 19 June 1997 (19.06.97) <b>(30) Priority Data:</b> 08/667,553      21 June 1996 (21.06.96)      US <b>(71) Applicant:</b> W. R. GRACE & CO.-CONN. [US/US]; 1114 Avenue of the Americas, New York, NY 10036 (US). <b>(72) Inventors:</b> DENTON, Dean, Alexander; 2602 Edgemere Avenue, Baltimore, MD 21229 (US). CARNEY, Michael, J.; 6351 Georgetown Boulevard, Eldersburg, MD 21784 (US). <b>(74) Agent:</b> MAGGIO, Robert, A.; W. R. Grace & Co.-Conn., 7500 Grace Drive, Columbia, MD 21044 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

**(54) Title:** AGGREGATE SUPPORTS AND OLEFIN POLYMERIZATION CATALYSTS SUPPORTED THEREON**(57) Abstract**

The present invention relates to a novel loose aggregate catalyst support composition characterized in that the aggregate has a surface area from about 100-1000m<sup>2</sup>/g, an average particle size of from about 5-250 microns, a pore volume of from about 0.5 to 3.0 cc/g in pores having pore diameters under 1000 Angstroms, and preferably having an AQI hardness of greater than 10, and wherein the aggregate particles comprise the following components: 1) porous solid particles from organic, inorganic oxide materials and mixtures thereof, said particles having an average particle size of less than 30 microns; and 2) a binder to loosely bind the particles from 1) together. In another embodiment, the catalytic support material of the present invention is combined with chromium compounds, Ziegler-Natta and Metallocene, or Ni based complexes, Pd based complexes catalytic materials resulting in catalytically active compositions when appropriately activated. Further disclosed are methods for making the support and catalysts and methods for using these compositions.



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AGGREGATE SUPPORTS AND OLEFIN POLYMERIZATION  
CATALYSTS SUPPORTED THEREON

5    BACKGROUND OF THE INVENTION

The present invention relates to novel aggregate support compositions that are particularly useful for polyolefin polymerization catalysts. The present invention further relates to a novel method for making the novel aggregate support composition.

Using different support materials with different physical characteristics is known  
10   in the art. Agglomerated catalytic support materials and catalysts have been prepared by a variety of methods. For example, Grace Davison, a business unit of W.R. Grace & Co. currently offers several agglomerated catalytic support materials that are prepared by spraying drying an aqueous slurry of various sizes of milled particles of silica hydrogels, e.g., Davison 948. These products typically have an AQI of less than 10. Additionally,  
15   U.S. Patent No. 4,228,260 discloses a process for preparing a porous pure silica suitable for use with chromium oxide catalysts. The process described therein is of converting a silicon-halogen compound to a non-porous silica by flame hydrolysis and then admixing with water to form a silica gel. The gel is then spray dried to achieve the required particle size and pore volume. U.S. Patent No. 4,657,880 discloses a high surface area  
20   agglomerate of porous silica particles wherein the particle is sintered to provide appreciable density and strength. U.S. Patent 4,902,666 discloses a method to prepare strong spheroidal solid agglomerates, typically 1-5 mm, containing alumina or a mixture of alumina and at least one other inorganic material. These agglomerates are formed from micron-sized particles fused together to make polylobed agglomerate particles having a  
25   diameter of 0.5mm or larger. U.S. Patent No. 4,704,374 discloses a method of making large spheroidal silica particulates produced from a mixture of xerogel or aerogel with silica hydrosol. These are particles from 1-10 mm in size and have a pore volume of 0.05 to 1.1 cc/g in pores having a pore diameter of less than 1000 Angstroms. Consequently, the thus produced particle is a large mechanically strong particle that is predominantly  
30   silica material.

Each support must typically be selected in view of the final polymer sought.

Small primary particle size is desirable to reduce faults and blemishes in the polymer product from silica residues. Severe milling of hydrogel, which produces a broad particle size distribution, will reduce primary particle size, but can reduce the pore volume below acceptable levels for use as a catalyst. Use of small catalyst particles (i.e., 5-10 microns) increases catalytic activity. However, slurry loop and gas phase polymerization processes require larger particle size (40-100 microns and above) for optimum operation. Accordingly, an ideal catalyst would combine small particle size attributes in a larger, more readily handled catalyst particle.

The present invention relates to a novel method of producing a novel catalyst aggregate support and catalyst material having macroporosity and that provides an active catalytic particle that is more active than the typical agglomerated support materials. It is believed the aggregate particles of the present invention fragment readily in the polymerization reactor, leading to high activity. This novel aggregate particle further combines the benefits of a large particle for handling purposes and a small particle and narrow particle size distribution for polymer reactor purposes leading to a more homogenous polymer (with respect to molecular weight and composition) having better film appearance.

## SUMMARY OF INVENTION

One embodiment of the present invention is a novel loose aggregate catalyst support composition characterized in that the aggregate has a surface area from about 100-1000m<sup>2</sup>/g, an average particle size of from about 5-250 microns, a pore volume of from about 0.5 to 3.0 cc/g in pores having pore diameters under 1000 Angstroms, and preferably having an AQI hardness of greater than 10, and wherein the aggregate particles comprise the following components:

- 1) porous solid particles from organic, inorganic oxide materials and mixtures thereof, said particles having an average particle size of less than 30 microns; and
- 2) a binder to loosely bind the particles from 1) together.

In another embodiment, the catalytic support material of the present invention is combined with chromium compounds, Ziegler-Natta, Metallocene, Ni based complexes,

Pd based complexes catalytic materials and mixtures thereof resulting in catalytically active compositions when appropriately activated.

Additional embodiments of the present invention are the methods of producing loose aggregate support materials and catalysts.

5           The method of producing the loose aggregate support composition comprises the following steps:

1)       prepare a slurry in a suitable solvent, preferably water, of the support material(s), said support materials having an average particle size of less than 30 microns, and the binder, such that on a weight basis of the slurry, the support material is from about  
10   5 to 40 wt.% and the binder is from about 10 to about 45 wt.% , and the remaining being the solvent used; and

2)       spray dry the slurry from step 1) to create the loose aggregate having a surface area of from about 100-1000 m<sup>2</sup>/g, an average particle size of from 5-250 microns, having a pore volume of from about 0.5 to 3.0 cc/g in pores having pore diameters under  
15   1000 Angstroms, and preferably having an AQI hardness of greater than 10.

The present invention further includes polymers produced using the catalyst systems described herein.

## DETAILED DESCRIPTION OF THE INVENTION

### 20   The Support Composition

One embodiment of the present invention is a novel loose aggregate catalyst support composition characterized in that the aggregate has a surface area from about 100-1000m<sup>2</sup>/g, preferably from about 150-800 m<sup>2</sup>/g, and more preferably from 200-700 m<sup>2</sup>/g. The aggregate has an average particle size of from 5-250 microns, preferably of  
25   from 10-120 microns, and a pore volume of from 0.50 to 3.0 cc/g in pores having pore diameters under about 1000 Angstroms, and preferably, an AQI hardness of greater than 10, preferably of from 15-70.

The aggregate particles comprise the following components

1)       solid porous particles from organic, inorganic, inorganic oxide materials  
30   and mixtures thereof (also referred to herein as support particles), said particles having an average particle size of less than 30 microns, preferably of from 1-25 microns, and most

preferably of from 1-10 microns; in the most preferred embodiment, the particle size distribution of the support particles is preferable such that 10% are at least 1 micron, 50% are less than 5 microns, and 90% are less than 9 microns.

2) a binder to loosely bind the particles from 1) together.

5 The support particles can be any sufficiently porous inorganic oxide, organic materials and mixtures thereof.

Inorganic oxide support materials include talcs, silicas, titania, silica chromia, silica chromia titania, silica-alumina, silica-titania, silica-titania-alumina, zirconia, silanized silica, aluminium phosphate gels and mixtures thereof. Preferred support  
10 materials are silica hydrogels, silica xerogels, silica aerogels, silica cogels and tergels (e.g., Si-Cr-Ti, Si-Ti and Si-Cr gels). Additional suitable silicas include silanized, fumed or precipitated silicas.

In general, silica hydrogels (a.k.a. aquagels) are silica gels formed in a liquid medium which has its pores filled with that liquid medium. A xerogel is a hydrogel with  
15 the liquid medium removed. An aerogel is a special type of xerogel which has the liquid removed in a manner that prevents the collapsing of the pore or a change in the pore structure. Colloidal or hydrosol silica are terms that refer to stable dispersions or sols of discrete particles of amorphous silicas. Precipitated silica is formed when the ultimate silica particles are coagulated as loose aggregates in an aqueous medium, recovered,  
20 washed and dried. Fumed silica (a.k.a., aerosils) is a powdered silica made by condensing silica from the vapor phase at elevated temperatures. Silanized silica can be any silica wherein any of the hydrogens in the hydroxy groups in the silica structure are replaced with  $\text{SiR}_3$ , where the R is a hydrogen and/or alkyl groups, thereby silanizing Si in the base silica.

25 Organic support materials include resinous material such as styrene-divinylbenzene copolymers, polyethylene, linear low density polyethylene, polypropylene, polyvinylchloride, polyvinylalcohol, poly-4-methyl-1-pentene, substituted polystyrenes and polyacrylates, starches, carbon and mixtures thereof.

Preferably, the support particles are compositions conventionally used as catalyst  
30 support materials. The degree of porosity in the support may be any level that is achievable in the starting material and desirable in the finished product. Preferably, the

support particles of the present invention have a pore volume of at least 0.5 cc/g; preferably more than 0.8 cc/g; and more preferably from about 1.1 to 3 cc/g.

Pore volume and surface area, for example can be measured from volume of nitrogen gas adsorbed in accordance with the BET method.

5           The binder material suitable for use in this invention is a binder that can be spray dried and that will continue to hold together the support particles in a loose aggregate as defined above. The binder is preferably selected from the group of silica oxide materials having from 5-100% by weight solids. These silica oxide materials can be hydrogels, hydrosol, fumed silica, precipitated silica, aluminium sols, and mixtures thereof,  
10       preferably milled hydrogels. Other suitable binder materials include silica co-gels or tergels containing chromium, aluminium, titanium and mixtures thereof. For example, U.S. Patent No. 3,887,494 teaches one method preparing SiO<sub>2</sub>- TiO<sub>2</sub> cogel. Preparation of these silicas are well known to those of ordinary skill. Many may be purchased from various suppliers such as Grace Davison, a business unit of W.R. Grace & Co. Fumed  
15       silica is available from Cabot Corp. under the "Cab-o-sil" name.

The binder may have particles within it and such particles should be of such a size to be compatible with the support particle size.

#### The Catalyst Composition

20           In another embodiment, the catalytic support material of the present invention is useful to support a variety of catalytically active materials such a Chromium, Ziegler-Natta, Metallocene, Ni based complexes, Pd based complexes catalyst systems and mixtures thereof.

Chromium catalyst can be made by several methods. For example, a chromium  
25       containing silica gel (e.g., Si-Cr co-gels or Ti-Cr-Si tergels) can be used as the starting support particle; alternatively, a chromium containing solution can be added to the slurry (before spray drying, e.g., in step 1). Chromium catalysts can be also be prepared by impregnating the aggregate support with a solution of chromium oxide, a compound that can be converted into chromium oxide or a composition containing chromium oxide,  
30       drying the impregnated aggregate particles and activating the catalyst composition between 400-1000°C. Preferable compounds that can be converted into chromium oxide

include chromium acetate, chromium nitrate, chromium acetylacetonate and mixtures thereof.

Co-gels such as Ti-Si and tergels such as Ti-Cr-Si can be used as the starting support materials to prepare a support for use as in Ziegler-Natta catalytic systems. In addition, Ziegler Natta, Ni based complexes, Pd based complexes and metallocene catalysts species can likewise be impregnated onto the aggregate particles using well known techniques depending on the final catalytic system desired.

#### The Method of Making the Support Aggregate

The method of producing the loose aggregate support composition comprises the following steps:

1) preparing a slurry in a suitable solvent of the support materials as described above having a pH that can be basic, neutral or acidic depending on the support particles and binder selected. Preferably, the pH is from 2-9, with the preferred pH from 7-8. The slurry may optionally contain manufacturing aids such as surfactants. The slurry is preferably from 35-90% by weight solvent and has a solids content of from 10-65% by weight, preferably from 10-40 Wt. % solids, and most preferably from 10-20 Wt.% solids.

Suitable solvents include water, hydrocarbons (including C5-C10 alkanes, preferably heptane, hexane, and octanes); aromatics (preferably toluene and benzene); alcohols, glycol ethers and esters, (preferably as isopropyl alcohol, hexanol, n-butoxy propanol, t-butoxy propanol; ethoxy ethyl acetate, methoxy propyl acetates, and ethoxy ethyl propionate); and mixtures of the foregoing. The preferred solvent is water.

Processing aids such as surfactants can be added to the slurry when needed. One suitable surfactant is Igepal®, a proprietary polyethylene glycol composition that can be purchased from Rhone Poulenc Corp.

2) Spray dry the slurry from step 1) to create the loose aggregate particles described above.

Optional steps include milling the starting material before preparing the slurry with the binder. The type of milling will depend on the starting material and the desired final product. Typical milling operations are well known wet and dry milling procedures. Additional optional steps include milling the binder material separately before adding to



the slurry and/or either stirring, mixing or milling the slurry after the support particles and binder are combined. These are process options that must be determined based on the materials used and the applications of the final product. The necessity of these for a given selection of materials can be determined without undue experimentation.

5           For example, depending on the silica binder used, it may be desirable to mill the slurry (or the binder separately) to act as a more efficient binder system.

          Furthermore, it may be desirable to calcine the resulting aggregate to remove any residual water for certain applications, e.g., when the aggregate is used to support Ziegler-Natta and/or Metallocene catalyst systems. Typical calcination can be carried out at 150 -  
10   900 °C for up to 24 hours.

          Ziegler-Natta, Metallocene, and Ni, Pd based complexes catalysts, cocatalyst and activator components can be impregnated in and on the supports of the present invention using any number of known techniques. Where suitable (e.g., non-aqueous slurries) the catalytic components can be added to the slurry before spray drying. Typically, the  
15   components are deposited on the aggregate after calcining. With respect to Ziegler-Natta catalyst system it is possible to use metal oxide -silica gels as the source of the active catalyst metal source, e.g. titania containing silica cogels or tergels .

          "Metallocene" is defined as an organometallic compound having a transition metal, including rare earth metals, in coordination with members of at least one five-  
20   member carbon ring, heterosubstituted five-member carbon ring, or a bridged (ansa) ligand defined as two cyclic moieties capable of coordinating to the transition or rare earth metals. Wherein the ansa bridge B, can be carbon, silicon, phosphorus, sulfur, oxygen, nitrogen, germanium, species such as CH<sub>2</sub>CH<sub>2</sub> (ethylene), Me<sub>2</sub>Si (dimethylsilyl), Ph<sub>2</sub>Si (diphenylsilyl) Me<sub>2</sub>C (isopropylidene), Ph<sub>2</sub>P (diphenylphosphoryl) Me<sub>2</sub>SiSiMe<sub>2</sub>  
25   (tetramethyldisilane) and the like. In particular, preferred metallocenes are derivatives of a cyclopentadiene (Cp), including cyclopentadienyl, substituted cyclopentadienyls, indenyl, fluorenyl, tetrahydroindenyl, and 1,1-disubstituted silacyclopentadienes, phosphocyclopentadienes, 1-metallocyclopenta-2,4-dienes, bis(indenyl)ethane and mixtures thereof. Metallocene catalyst are typically activated by combining the active  
30   metal specie with borate or aluminoxane compounds well known in the art.

The transition metal component of the metallocene is selected from Groups IIIB through Group VIII of the Periodic Table and mixtures thereof, preferably Group IIIB, IVB, VB, VIB and rare earth (i.e., lanthanides and actinides) metals, and most preferably titanium, zirconium, hafnium, chromium, vanadium, samarium and neodymium. Of these

5 Ti, Zr, and Hf are most preferable.

"Ziegler-Natta" ("ZN") is defined as a transition metal (Group IIIB through VIIB) halide, alkyl, aryl, or alkoxy compounds and mixtures thereof in combination with a Group I through III elements of the Periodic Table. A typical example is  $\text{TiCl}_4$  and  $\text{AlEt}_3$ . Preferred Ziegler-Natta systems are those employing a complex of magnesium

10 chloride/titanium halide or alkoxy compound and an aluminum alkyl deposited on the novel supports of this invention. Methods of producing catalysts are known in the art. Electron donors may also be used in Ziegler-Natta catalysts systems of the present invention and include, esters, ethers, amines, silanes and alcohols and mixtures thereof.

It is also believed that the compositions and methods described herein are suitable

15 for use with catalysis that are palladium and nickel-based complexes (e.g., Ni, Pd coordinated to diimine (non-cyclopentadienyl, nitrogen-containing) ligands) described in Brookhart, Johnson, and Killian, J. Am Chem. Soc., 117, 6414 (1995). Typical versions of these catalysts are cationic and can be activated in ways similar to metallocenes using aluminoxane or borate co-catalysts.

Catalyst systems supported on the aggregate described herein are useful to produce

20 polymers using solution polymerization, slurry polymerization or gas phase polymerization techniques. As used herein the term polymerization includes copolymerization and terpolymerization and the terms olefins and olefinic monomers include olefins, alpha-olefins, diolefins, styrenic monomers, acetylenically unsaturated

25 monomers, cyclic olefins and mixtures thereof.

Methods and apparatus for effecting such polymerization reactions are well known. The catalyst according to the present invention can be used in similar amounts and under similar conditions known to olefin polymerization catalysts. Typically for the slurry process, the temperature is from approximately 0 °C to just below the temperature

30 at which the polymer becomes soluble in the polymerization medium. For the gas phase

process, the temperature is from approximately 0°C to just below the melting point of the polymer. For the solution process, the temperature is typically the temperature from which the polymer is soluble in the reaction medium up to approximately 275°C.

The pressure used can be selected from a relatively wide range of suitable pressures, e.g., from subatmospheric to about 20,000 psi. Suitable pressure is from atmospheric to about 1000 psi, and most preferred from 50 to 550 psi. In the slurry or particle form process, the process is suitably performed with a liquid inert diluent such as a saturated aliphatic hydrocarbon. The hydrocarbon is a C<sub>4</sub> to C<sub>10</sub> hydrocarbon, e.g., isobutane or an aromatic hydrocarbon liquid such as benzene, toluene or xylene. The polymer is recovered directly from the gas phase process or by filtration or evaporation from the slurry process or evaporation of solvent from the solution process.

The support and catalyst system of the present invention is particularly suited for the gas phase and slurry phase polymerization processes and particularly useful for the production of polyethylene and polypropylene.

#### 15 Figures

Figures 1-4 are electron microscope photographs of one embodiment of the present invention and of a spray dried agglomerated silica.

Figure 1 is a photographic image of particles from one embodiment (silica hydrogel support and milled silica hydrogel as binder) of the present invention. The photograph was taken with an electron microscope and represents a 500x magnification of the actual particles.

Figure 2 is a photographic image of particles made by spray drying of an aqueous mixture of hydrogel and silica and is typical of Davison 948. The photograph was taken with an electron microscope and represents a 500x magnification of the actual particles.

Figure 3 is a photographic image of particles from one embodiment (silica hydrogel support and milled silica hydrogel as binder) of the present invention. The photograph was taken with an electron microscope and represents a 10,000x magnification of the actual particles.

Figure 4 is a photographic image of particles made by spray drying of an aqueous mixture of hydrogel and silica and is typical of Davison 948. The photograph was taken

with an electron microscope and represents a 10,000x magnification of the actual particles.

Figure 5 is a schematic illustration of the apparatus used in the AQI test.

5

### EXAMPLES

The examples below are illustrative of preferred embodiments of the present invention and are not meant to limit the scope of the claim herein.

Each of the following examples was prepared as follows, with the specific information for each material, and characteristics provided in Table 1. The novel supports  
10 of this invention were prepared by the novel process described herein. In particular, the slurries containing the support and binder materials of desired particle sizes were typically blended until a uniform mixture was obtained. The amount of support, binder and solvent used was selected to achieve the wt.% ratio of support to binder provided in Table 1. Water was the solvent used in each example.

15 The slurries (having a average particle size of under 30 microns) were then spary dried. With respect to examples 6 and 8, the binder was coarsely ground before being mixed with the support material. The mixtures of support and binder materials were then comilled to prepare the spray dryer feed having an average particle size of under 10 microns (and 90% under 30 microns). A Niro spray dryer was used at the manufacture's  
20 standard operating conditions.

Catalysts were prepared by impregnating the aggregate support material thus made as provided in Tables 2 and 3. The polymers were obtained under the conditions provided below using a 2-liter Zipperclave reactor (constant temperature and pressure).

Table 1. Description of Aggregate Support

Example	Support Material	Support Part. Size APS/ 90%		Binder Material	wt % Support: Binder	Surface Area (m <sup>2</sup> /g)	Pore Volume (cc/g)	AQI
1	Aerogel	5μ	10 μ	Hydrogel	12:4	382	1.62	41
2	Aerogel	3μ	5 μ	Hydrogel	9.75:3.25	381	1.56	31
3	Azeo. Cogel Aerogel #	5.2 μ	8 μ	Hydrogel*	10.7:3.5	395	1.44	48
4	Azeo. Cogel Aerogel #	5.2 μ	8 μ	Si/Ti Cogel **	8:4	427	1.39	67
5	Cogel Aerogel	4.6 μ	9 μ	Si/Ti Cogel **	11.8:3.93	373	1.15	36
6	Aerogel	5.3 μ	8 μ	Hydrogel	12.5:4.2	322	1.61	53
7	Aerogel	5.3 μ	10 μ	Fumed Silica ***	13.8:3.4	364	1.63	53
8	Aerogel	4.6 μ	28 μ	Hydrogel	10.0:3.7	573	1.34	65
9	Precipitated Silica	5 μ	12 μ	Precipitated Silica Slurry	7.5:2.5	476	1.27	34

Notes:

5

Aerogels, cogels and precipitated silicas are available from Grace Davison, a business unit of W.R. Grace & Co. Except where noted, the binder materials are from the same base gel used to prepare the support (i.e., aerogels) materials.

Binders were typically 35 wt % solid, 65 wt % water.

10

\*Silica hydrogel used in Example 3 was the same as that used in Example 6.

\*\*Si/Ti Cogel binder used in Examples 4 and 5 was prepared by milling cogel hydrogel (nominal surface area = 400 m<sup>2</sup>/g, pore volume = 1.1 cc/g).

15

\*\*\* Fumed silica purchased from Cabot Corp., "Cab-o-Sil."

# Azeotropically dried Cogel of Silica/Ti.

Catalyst Example 10.

10.0 grams of support Example 1, previously calcined at 600 °C for 4 hours, was slurried in 50 mL of heptane. Dibutylmagnesium (20 mmol) was added dropwise and the slurry was stirred for 1 hour. Anhydrous hydrogen chloride was bubbled through the suspension for 10 minutes (or until an aliquot of the suspension was slightly acidic). Excess HCl was removed by purging the flask with argon for 10 minutes. The off-white slurry was treated with 2.9 mmol of TiCl<sub>4</sub> and stirred for 1 hour. Diethylaluminum chloride (DEAC, 25 mmol) was added dropwise and stirring continued for 2 hours. Volatiles were removed under vacuum to yield a free-flowing powder.

Catalyst Example 11. Prepared using the same procedure as Example 10 except employing 10.0 grams of support Example 2, previously calcined at 600 °C for 4 hours.

Catalyst Example 12. Prepared using the same procedure as Example 10 except employing 10.0 grams of support Example 7, previously calcined at 600 °C for 4 hours.

Catalyst Example 13. Prepared using the same procedure as Example 10 except employing 10.0 grams of support Example 9, previously calcined at 600 °C for 4 hours.

Catalyst Example 14. Prepared using the same general procedure as Example 13 except employing the following amounts of reagents: 25.0 mmol of dibutylmagnesium; 3.6 mmol of TiCl<sub>4</sub>; 31.0 mmol of DEAC.

Catalyst Example 15. Prepared using the same procedure as Example 10 except employing 10.0 grams of support Example 8, previously calcined at 600 °C for 4 hours.

Catalyst Example 16. Prepared using the same procedure general procedure as Example 15 except employing the following amounts of reagents: 40.0 mmol of dibutylmagnesium; 5.8 mmol of TiCl<sub>4</sub>; 50.0 mmol of DEAC.

Catalyst Example 17. Prepared using the same general procedure as Example 10 except employing 10.0 grams of support Example 8, previously calcined at 600 °C for 4 hours, and the following amounts of reagents: 25.0 mmol of dibutylmagnesium; 5.6 mmol of TiCl<sub>4</sub>; 50.0 mmol of DEAC. Prior to removal of volatiles, 0.2 mL of 2,6-lutidine was added and the resulting slurry was stirred an additional 1 hour. Drying under vacuum again produced a free-flowing powder.

Comparative Example CE1. Prepared using the same procedure as Example 10 except employing 10.0 grams of Sylopol 948 previously calcined at 600 °C for 4 hours.

Comparative Example CE2. Prepared using the same procedure as Example CE1 except employing the following amounts of reagents: 40.0 mmol of dibutylmagnesium; 5.8 mmol of  $\text{TiCl}_4$ ; 50.0 mmol of DEAC.

Table 2

5

## Description of the Catalyst Made and Polymer

Example	Support Example	% Mg	% Ti	%Al	Rx T (°C)	Activity	MI	HLMI	MFR
10	1	3.35	0.66	4.35	75	5400	0.97	38.4	39.5
11	2	3.41	0.69	3.9	75	5510	1.23	51.1	41.6
12	7	3.42	0.68	4.24	75	5040	1.04	39.3	37.8
13	9	2.92	0.6	3.62	75	4770	1.27	50.7	39.9
14	9	3.93	0.78	4.72	75	4430	1.4	55.2	39.4
15	8	3.51	0.71	4.31	75	4770	0.94	34.3	36.5
16	8	5.29	1.07	6.05	75	8710	0.69	24.7	35.8
17	8	3.18	1.05	6.47	75	5980	0.61	18.8	30.8
CE1	Sylopol 948	3.14	0.72	4.13	75	3300	0.55	20.8	37.8
CE2	Sylopol 948	5.14	1.05	5.8	75	3760	1.02	40.2	39.5

General Synthetic Procedures. In catalyst preparation, Schlenk and glove box techniques were used throughout to exclude water and oxygen. All solvents were thoroughly dried and degassed prior to use.

Examples 10-17 & Comparative Examples, CE1 & 2: Polymerizations performed at 75 °C, 60 psig  $\text{H}_2$  partial pressure, 120 psig ethylene partial pressure. Catalyst amounts varied between 15-50 mg, corresponding to between 4.5 and 7.5 micromoles of Ti.

Polymerizations were initiated by addition of 0.75 millimoles of triisobutyl aluminum (TiBAI). Activity is expressed as g polymer/g catalyst-hr.

Catalyst Example 18: 10.0 grams of the agglomerated cogel support Example 4 was slurried in 50 mL of heptane and treated with 20 mmol of butylethylmagnesium. Stirring was continued for 1 hour. Chlorotrimethylsilane (9 mL) was added and stirred for 30 minutes. Boron trichloride (20 mmol) was added slowly and stirring continued for an additional hour. The resulting solid was collected on a frit, washed twice with 50 mL of pentane and dried under vacuum at room temperature.

Catalyst Examples 19 and 20. Same general procedure for Example 18 except that 0.3 mL of 2,6-lutidine was added subsequent to boron trichloride and stirred an additional

hour. The resulting solid was collected on a frit, washed twice with 50 mL of pentane and dried under vacuum at room temperature.

Table 3

5

Example	Support Example	% Mg	% Ti	Rx T (°C)	Activity	MI	HLMI	MFR
18	4	3.24	1.73	75	3450	1.66	60.9	36.7
19	4	3.07	1.72	75	2180	0.65	18.4	28.1
20	4	3.07	1.72	85	2470	1.9	50.1	26.4

Examples 17-19 (Table 3): Polymerizations performed at the indicated temperature, 60 psig H<sub>2</sub> partial pressure, 120 psig ethylene partial pressure. Polymerizations were initiated by addition of 50 mg of catalyst and 0.75 millimoles of TiBAI. Activity is expressed as g polymer/g catalyst-hr.

10

The Melt index of the final resin was determined using ASTM Proc D1238, Cond.E, Procedure A; High Load Melt Index by ASTM Proc. D1238, Cond. F, Procedure B; MFR is calculated by dividing the HLMI by the MI.

The AQI (Attrition Quality Test) is a Grace Davison test used to rank the hardness of a material. The quality index is a measure of the material's resistance to particle size reduction under controlled conditions of turbulent motion. AQI represents the weight percent of the over 16 micron size fraction which is reduced to particle sizes less than 16 microns under the test conditions.

15

The baseline of the 0-16 micron fraction is determined by the Mastersizer (tradename of Malvern Corp) particle size analyzer. A 5 gram sample of material is placed in a covered cup subjected to a tangential jet of air at a rate of 9 liters per minute at a 60% Relative Humidity introduced through an orifice fixed at the bottom of the covered cup for a period of 30 minutes. The fines generated by the attrition mechanism and the coarse particles left in the cup after attrition are combined and mixed. The percent of 0-16 micron fines after attrition are then determined on the mixture by the Mastersizer particle size analyzer. A schematic illustration of the equipment used in this test is provided in Figure 5.

20

25



The calculation is as follows.

$AQI = \% \text{ less than } 16 \text{ microns} \text{ minus } \% \text{ less than } 16 \text{ microns pre-attrition test.}$

We Claim:

1. A loose aggregate catalyst support composition characterized in that the aggregate has a particle size of from 5-250 microns, a surface area of from about 100 -  
5 1000 m<sup>2</sup>/g and an AQI hardness of greater than 10, said aggregate particles comprising:
  - 1) loosely bound support particles formed from solid support particles selected from the group consisting of organic and inorganic oxide materials and mixtures thereof, said support particles having an average particle size of less than 30 microns; and
  - 2) a binder to loosely bind the particles from step 1) together.
- 10 2. The aggregate composition of claim 1 wherein the support particles are selected from the group consisting of talcs, silicas, titania, silica-alumina, silica-chromia, silica-chromia-titania, silica-titania, silica-titania-alumina, zirconia, silanized silica, aluminium phosphate gels, styrene-divinylbenzene copolymers, polyethylene, linear low  
15 density polyethylene, polypropylene, polyvinylchloride, polyvinylalcohol, poly-4-methyl-1-pentene, substituted polystyrenes and polyacrylates, starches, carbon and mixtures thereof; and the binder is selected from the group consisting of silica hydrogels, silica cogels and tergels, silica hydrosol, fumed silica, precipitated silica and mixtures thereof.
- 20 3. The aggregate composition of claim 2, wherein the support particles have an average particle size of from 5 to 25 microns, and the aggregate composition has an AQI of from 15-70 and a surface area of from 150-800 m<sup>2</sup>/g.
- 25 4. The aggregate composition of claim 3, wherein the support particles have an average particle size of from 1 to 10 microns, and the aggregate composition has a surface area of from 200-700 m<sup>2</sup>/g.

5. The method of producing a loose aggregate support composition, said method comprising the following steps:

- 1) preparing a slurry of support particles, wherein the average size of the support particles is less than 30 microns, in a solvent with a binder; and
- 5 2) spray drying the slurry from step 1) to create the loose aggregate having a surface area from about 100 - 1000 m<sup>2</sup>/g, and a particle size of from 5 -250 microns.

6. The method of claim 5 wherein the method further comprises the steps of selecting the support particles from the group consisting of talcs, silicas, titania, silica-  
10 alumina, silica-chromia, silica-chromia-titania, silica-titania, silica-titania-alumina, zirconia, silanized silica, aluminium phosphate gels, styrene-divinylbenzene copolymers, polyethylene, linear low density polyethylene, polypropylene, polyvinylchloride, polyvinylalcohol, poly-4-methyl-1-pentene, substituted polystyrenes and polyacrylates, starches, carbon and mixtures thereof; and the binder from the group consisting of silica  
15 hydrogels, silica cogels and tergels, silica hydrosol, fumed silica, precipitated silica and mixtures thereof.

7. The method of claim 6 wherein the method further comprises the step wherein the solvent is selected from water, C5 -C10 hydrocarbons, aromatics, alcohols,  
20 glycol ethers, esters and mixtures of the foregoing.

8. A catalyst composition comprising:

A) a loose aggregate catalysts support composition characterized in that the aggregate has a particle size of from 5 - 250 microns, a surface area of from about 100 - 1000 m<sup>2</sup>/g and an AQI hardness of greater than 10, said aggregate particles comprising:

- 5           1) loosely bound support particles formed from solid support particles selected from the group consisting of organic and inorganic oxide materials and mixtures thereof, said support particles having an average particle size of less than 30 microns;
- 2) a binder to loosely bind the particles from step 1) together; and
- B) a catalytically active metal component selected from group of chromium  
10 compounds, Ziegler-Nattas, metallocenes, Ni based complexes, Pd based complexes and mixtures thereof.

9. The catalyst composition of claim 8 wherein the support particles are selected from the group consisting of talcs, silicas, titania, silica-alumina, silica-titania,  
15 silica-chromia, silica-chromia-titania, silica-titania-alumina, zirconia, silanized silica, aluminium phosphate gels, styrene-divinylbenzene copolymers, polyethylene, linear low density polyethylene, polypropylene, polyvinylchloride, polyvinylalcohol, poly-4-methyl-1-pentene, substituted polystyrenes and polyacrylates, starches, carbon and mixtures thereof; the binder is selected from the group consisting of silica hydrogels, silica cogels  
20 and tergels, silica hydrosol, fumed silica, precipitated silica and mixtures thereof; and the catalytically active material is selected from the organometallic compounds having a transition metal, including rare earth metals, in coordination with members of at least one five-member carbon ring, heterosubstituted five-member carbon ring, or a bridged (ansa) ligand defined as two cyclic moieties capable of coordinating to the transition or rare  
25 earth metals; a Group IIIB through VIIIB transition metal halide, alkyl, aryl, or alkoxy compounds and mixtures thereof in combination with a Group I through III elements; chromium acetate, chromium nitrate, chromium actylacetate, Ni based complexes, Pd based complexes and mixtures of any of the forgoing catalytically active materials.

10. The catalyst composition of claim 9, wherein the support particles have an average particle size of from 1 to 25 microns, and the aggregate composition has an AQI of from 15 to 70 and a surface area of from 150-800 m<sup>2</sup>/g.

5 11. The catalyst composition of claim 10, wherein the support particles have an average particle size of from 1 to 10 microns, and the aggregate composition has a surface area of from 200-700 m<sup>2</sup>/g.

12. The method of producing a catalyst composition, the method comprising  
10 the steps of:

1) prepare a slurry of support particles, wherein the average size of the support particles is less than 30 microns, in a solvent with a binder;

2) spray dry the slurry from step 1) to create the loose aggregate having a surface area from about 100 - 1000 m<sup>2</sup>/g, and a particle size of from 5 -250 microns; and  
15 and adding catalytically active material in one of the following ways:

3a) selecting the support particle for step 1) containing a catalytically active metal and, optionally, adding an appropriate co-catalysts or activator to the slurry before spray drying or by impregnation after spray drying;

3b) adding a catalytically active material before spraying drying and,  
20 optionally, adding an appropriate co-catalysts or activator to the slurry before spray drying or by impregnation after spray drying; and/or

3c) impregnating the loose aggregate following step 2) with a catalytically active material and, optionally, adding an appropriate co-catalyst or activator to the slurry before spray drying or by impregnation after spray drying.

13. The method of claim 12 wherein the method further comprises the steps of selecting the support particles from the group consisting of talcs, silicas, titania, silica-alumina, silica-titania, silica-chromia, silica-chromia-titania, silica-titania-alumina, zirconia, silanized silica, aluminium phosphate gels, styrene-divinylbenzene copolymers, polyethylene, linear low density polyethylene, polypropylene, polyvinylchloride, polyvinylalcohol, poly-4-methyl-1-pentene, substituted polystyrenes and polyacrylates, starches, carbon and mixtures thereof; and the binder from the group consisting of silica hydrogels, silica cogels and tergels, silica hydrosol, fumed silica, precipitated silica and mixtures thereof; and the catalytically active material is selected from the organometallic compounds having a transition metal, including rare earth metals, in coordination with members of at least one five-member carbon ring, heterosubstituted five-member carbon ring, or a bridged (ansa) ligand defined as two cyclic moieties capable of coordinating to the transition or rare earth metals; a Group IIIB through VIIB transition metal halide, alkyl, aryl, or alkoxy compounds and mixtures thereof in combination with a Group I through III elements; chromium acetate, chromium nitrate, chromium acetylacetonate, Ni based complexes, Pd based complexes and mixtures of any of the foregoing catalytically active materials.

14. The method of claim 13 wherein the method further comprises the step wherein the solvent is selected from water, C5 -C10 hydrocarbons, aromatics, alcohols, glycol ethers, esters and mixtures of the foregoing.

15. The composition produced by any of the methods of claims 5, 6, 7, 12, 13, or 14.

25

16. A polyolefin produced by a polymerization process comprising contacting one or more monomers polymerizable under suitable polymerization conditions with a composition from claims 1, 2, 3, 4, 8, 9, 10, 11, 15 or produced according to the method of claims 5, 6, 7, 12, 13, or 14 in a reaction zone.

30

17. The polymer of claim 16 wherein the polymerization process is a slurry or gas polymerization process.

18. The polymer of claim 16 wherein the polymer produced is polyethylene or  
5 polypropylene.

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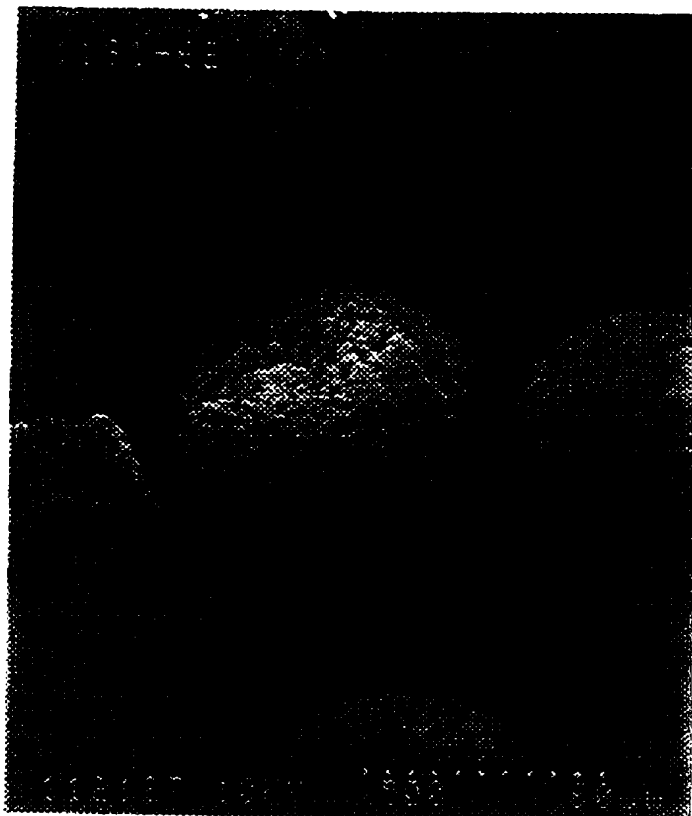


FIG. 1

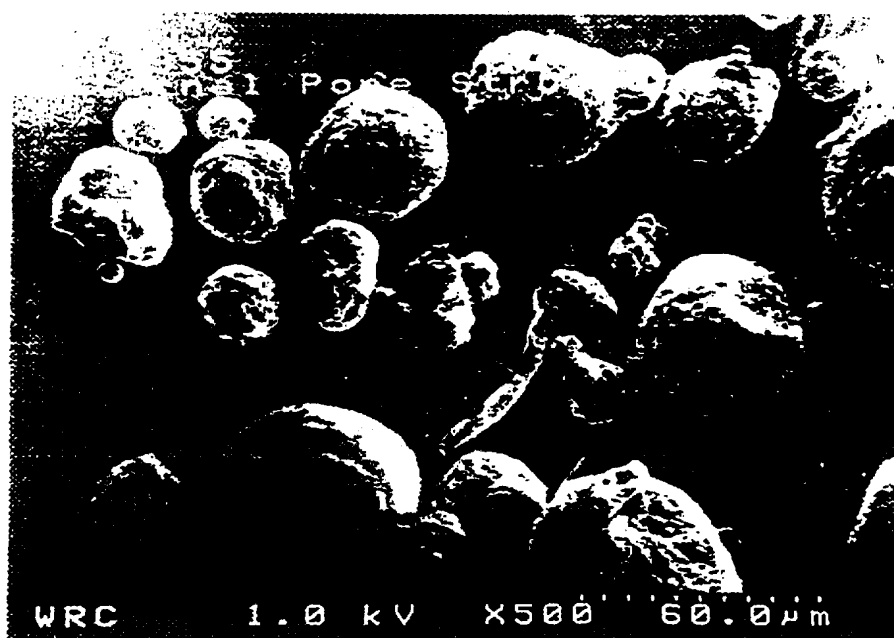


FIG. 2



2 / 3

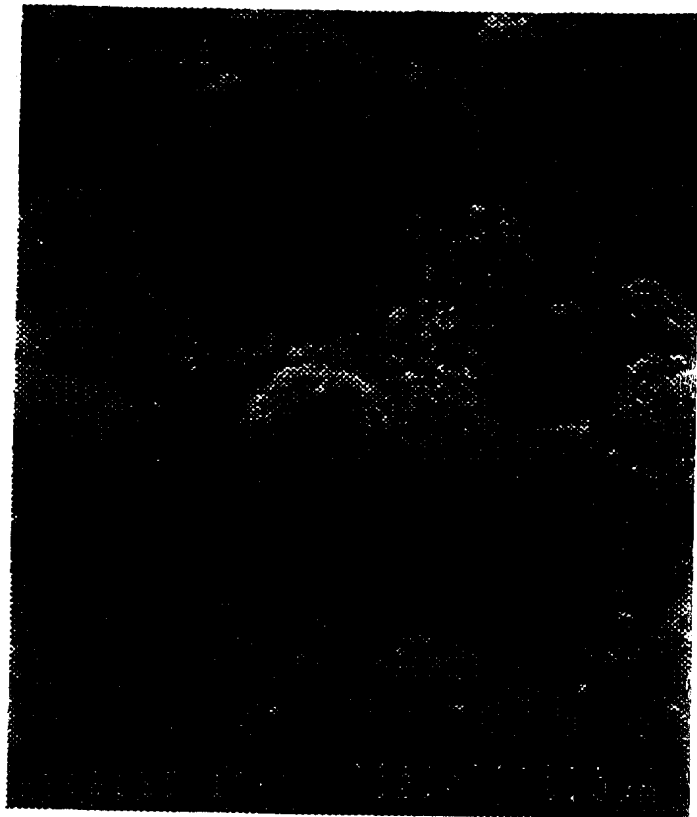


FIG.3

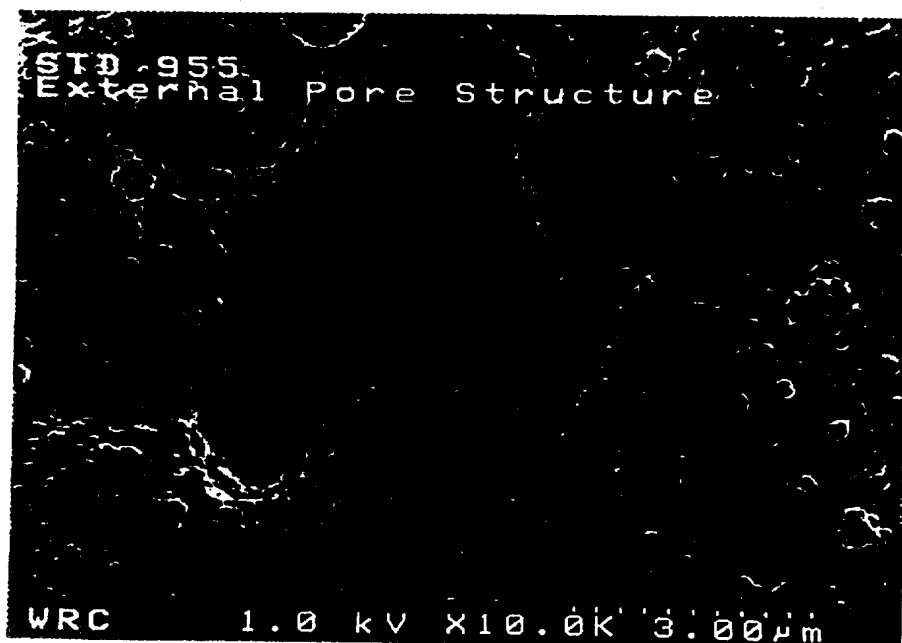
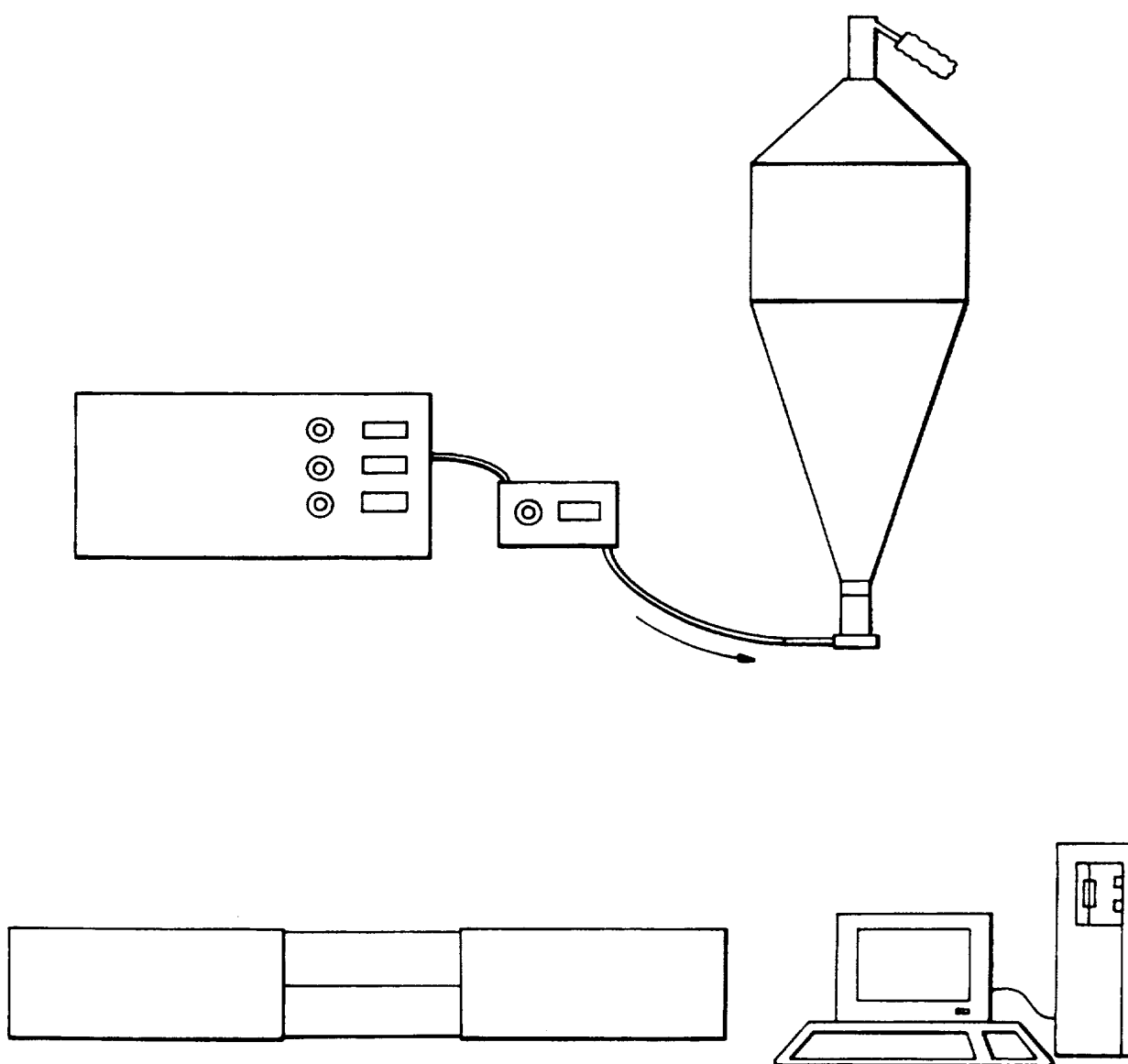


FIG.4

FIG. 5



# INTERNATIONAL SEARCH REPORT

Int. .ional Application No  
PCT/US 97/11951

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F10/00 C08F4/02 B01J37/00 B01J31/22

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 698 622 A (BP CHEM INT LTD) 28 February 1996 see page 2, line 15 - page 3, line 16; claims 1-12 ---	1-4,8-18
X	WO 93 23438 A (UNILEVER PLC ;UNILEVER NV (NL); JOSEPH CROSFIELD & SON LTD (GB)) 25 November 1993 see claims 11,34,36,37 ---	1-3, 5-10, 12-18
A	US 4 070 286 A (ILER RALPH KINGSLEY ET AL) 24 January 1978 see claim 1 ---	1,2
P,A	WO 96 34062 A (GRACE GMBH ;BELLIGOI PETER (DE); FIELD REX (DE); LUEERS GEORG (DE)) 31 October 1996 see page 6, line 3 - line 7; claims 1,6 -----	1,2,5



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents :

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Date of the actual completion of the international search

14 October 1997

Date of mailing of the international search report

23.10.97

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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